JP Laid-Open No. H9-52729

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-052729
(43)Date of publication of application : 25.02.1997

(51)Int.Cl. C03C 3/078
C03C 3/087
C03C 3/089
C03C 3/091
C03C 3/093
C03C 4/00

(21)Application number : 08-146256
(22)Date of filing : 07.06.1996

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(30)Priority
Priority number : 07143472 Priority date : 09.06.1995 Priority country : JP

## (54) SCUFFING RESISTANT GLASS

(57)Abstract:
PROBLEM TO BE SOLVED: To improve fragility, scuffing resistance and durability of glass by incorporating $SiO_2$, $RO+R'_2O$, $Li_2O$ and $M_2O_3$.
SOLUTION: 74-78wt.% $SiO_2$, 15-30wt.% $RO+R'_2O$ in which a wt. ratio of $RO/R'_2O$ is 0.6-1.6 (R is more than one kind selected among Mg, Ca and Zn and R' is more than one kind selected among Li, Na and K), ≥4wt.% $Li_2O$ and 0-10wt.% $M_2O_3$ (M is B and/or Al) are mixed and heated at 1,450-1,600° C to vitrify. Then, after clarifying this molten glass, the glass is formed in a prescribed shape to obtain the scuffing resistant glass having 2.41-2.47g/cc density, ≤6,700m1/2 B expressed by formula, B=Hv/Kc (B is an index value of the fragility, Hv is Vickers hardness and Kc is fracture toughness) and viscosity of 102 poise at ≤1,600° C.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

JAPANESE [JP,09-052729,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

* NOTICES *



1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

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CLAIMS

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[Claim(s)]
[Claim 1] essential -- 74 - 78% of the weight of SiO2, and RO/R' -- 15 - 30% of the weight of RO+R'2O (R -- Mg --) whose O-fold [ 2 ] quantitative ratios are 0.6-1.6 One or more sorts and R' which were chosen from calcium and Zn One or more sorts chosen from Li, Na, and K, Abrasion-proof nature glass characterized by consisting of 4% of the weight or more of Li2 O, and 0 - 10% of the weight of M2 O3 (one or more sorts as which M was chosen from B and aluminum), and carrying out a consistency in 2.47g/cc or less exceeding 2.41g/cc.
[Claim 2] Abrasion-proof nature glass according to claim 1 characterized by the brittleness index value B being 1/2 or less [ 6700m - ]. Here, they are B=Hv/Kc (Hv is Vickers hardness number and Kc is a fracture toughness value).
[Claim 3] Viscosity is 102. Abrasion-proof nature glass according to claim 1 or 2 characterized by the temperature used as a poise being 1600 degrees C or less.
[Claim 4] Abrasion-proof nature glass according to claim 1, 2, or 3 which essentially consists of the following components.
SiO2 74-78 Weight %, MgO 5-15 Weight %, CaO 0- 2 Weight %, ZnO 0- 2 Weight %, Li2 O 4-16 Weight %, Na2 O 0- 5 Weight %, K2 O 0- 7 Weight %, B-2 O3 0- 2 Weight %, aluminum 2O3 0- 2 Weight %.

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[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to glass with very high abrasion-proof nature.
[0002]
[Description of the Prior Art] Glass is essentially a weak ingredient, and if the reinforcement falls and the force is added there by the minute surface crack generated especially at the time of use, the crack which makes a minute blemish the start will extend and it will result in destruction.
[0003] Therefore, in order to raise the endurance of glass, the attempt which a blemish tends to make it hard to be attached to a front face is performed for many years. For example, it is surface hard coating, and is surface strengthening by the ion exchange, and is physical strengthening by quenching.
[0004] these techniques are divided roughly into the approach of covering the front face of glass with other ingredients, and preventing generating of a blemish, and the approach of making a front face generate compressive residual stress, and preventing generating of a blemish, and expansion — having — which — an imitation — it is not the attempt which essentially improves the brittleness of glass itself. Therefore, there is a problem that surface coating will not be removed by wear, degradation, etc. or the effectiveness is not discovered under the environment where surface residual stress disappears by the rise of temperature etc.
[0005] On the other hand, although current but the soda lime silica glass currently used widely have transition also historically, generally it has the following presentations.
[0006]
SiO2 66-75 Weight %, MgO 0- 5 Weight %, CaO 7-12 Weight %, Na2 O 12-20 Weight %, K2 O 0- 3 Weight %, aluminum 2O3 0- 4 Weight %.
[0007] In soda lime silica glass, there is not much research about the relation between a presentation and a degree of hardness. as general recognition — SiO2 That network affinity will go up if Na2 O is permuted by that reinforcement will go up if it is made to increase, and CaO, and reinforcement improves, and aluminum 2O3 It comes out that addition is useful to improvement in reinforcement and a degree of hardness etc. to some extent.
[0008] Although it is important when determining the reinforcement of the still more nearly actual glass about the abrasion degree of hardness corresponding to the ease of attaching of a surface blemish, the polish phenomenon of glass is complicated and is not necessarily good. [ of functionality with Vickers hardness ] This is considered because it has desorption from the sample by generating and expansion of not only a factor but a detailed crack related to a degree of hardness in abrasion-proof nature, and the influence by frictional heat.
[0009] After all, conventionally, there was only recognition of extent that abrasion-proof nature falls as quartz glass is most excellent in abrasion-proof nature and network modifiers increased in number about the relation between the ease of attaching of the blemish on the front face of glass, and a presentation.
[0010]
[Problem(s) to be Solved by the Invention] Based on the conventional recognition, it is SiO2 in order to raise a degree of hardness simply. If it is made to increase, since it will be hard coming to dissolve, production by scorification with sufficient productivity becomes difficult. On the other hand, in the glass of a soda lime silica system, generally, when production with scorification chooses an easy presentation, the improvement in a degree of hardness has so much the problem that it does not see.
[0011] Moreover, by performing a certain processing on the surface of glass, in the approach of conquering brittleness, the after treatment after glass shaping is required, and there are a problem of a rise of cost, a problem of a limit of application, a problem that the effectiveness does not maintain at the time of use depending on the case.
[0012] Production by scorification is possible for it, and the purpose of this invention is to offer the glass which maintained fundamentally the advantages, such as endurance which soda lime glass has, while it improves the not above-mentioned problem that the conventional technique has, i.e., reforming of after treatment or a front face, but the brittleness of glass itself and prevents generating of the blemish by the external force at the time of real use.
[0013]
[Means for Solving the Problem] this invention — essential — 74 - 78% of the weight of SiO2, and RO/R' — 15 - 30% of the weight of RO+R'2O (R — Mg —) whose 2O ratios are 0.6-1.6 One or more sorts and R' which were chosen from calcium and Zn One or more sorts chosen from Li, Na, and K, It is abrasion-proof nature glass characterized by consisting of 4% of the weight or more of Li2 O, and 0 - 10% of the weight of M2 O3 (one or more sorts as which M was chosen from B and aluminum), and carrying out a consistency in 2.47g/cc or less exceeding 2.41g/cc.
[0014] this invention person considers the presentation and the relation of abrasion-proof nature in a detail about various soda lime silica glass, and sets to glass presentation within the limits of the result above-mentioned. By carrying out the consistency exceeding 2.41g/cc in 2.47g/cc or less (the consistency of the usual soda lime silica glass being about 2.49-2.52g/cc) While maintaining fundamentally properties, such as melting nature in the conventional soda lime silica glass, and chemical durability, it found out that it was hard coming to attach a blemish very compared with the conventional soda lime silica glass.
[0015] When the consistency of glass was especially lowered from cc in 2.52g /by the above-mentioned presentation and it became [ cc ] in 2.47g /or less, it found out that abrasion-proof nature improved rapidly to other properties changing gradually. In a presentation region with a this of about 2.47g [/cc ], i.e., consistency, it thinks for the flexibility (degree of freedom of the bond

angle in atomic level) of glass structure to change rapidly.
[0016] That is, it is based on having found out that this invention was possible to presentation within the limits which whose consistency is the factor which influences abrasion-proof nature most in soda lime silica glass, and has the control. And if the presentation is optimized as shown in the after-mentioned example, the glass whose actual reinforcement the generating load of a blemish was very high and also improved greatly compared with the usual soda lime silica glass will be obtained easily [ manufacture by scorification ].
[0017] Next, the presentation range of the glass of this invention is explained.
[0018] SiO2 It is the principal component which forms the network structure of glass. Since a consistency rises and crack propagation becomes easy while the amount of non-bridging oxygen will increase relatively and the network structure will become weak, if there is too little this, the reinforcement itself becomes low. Moreover, if many [ too ], melting nature will worsen and it will become difficult to obtain homogeneous glass with scorification. By this invention, it may be 74 - 78 % of the weight to the whole glass in this viewpoint.
[0019] R'2O (one or more sorts as which R' was chosen from Li, Na, and K) is a component indispensable to a soluble improvement with RO (one or more sorts as which R was chosen from Mg, calcium, and Zn) indispensable to a soluble improvement and an improvement of chemical durability. The amount of R'2O and RO is made into 15 - 30 % of the weight with a total amount.
[0020] By carrying out constant-rate content of the RO, the chemical endurance of the whole glass is improvable. In this viewpoint, weight ratio RO/R'2O is set to 0.6-1.6 by this invention.
[0021] Such R to add and R' Small [ an element number ] as a general trend, a light element is effective in reduction of a consistency, and abrasion-proof nature is also improved as a result. It is desirable to make [ many ] Mg as R rather than calcium in this viewpoint. However, there are some which also show different behavior under the effect of the element added by coincidence in some elements. These are considered because there are a form of the network structure where the factor which determines abrasion-proof nature makes a subject the amount of non-bridging oxygen and a silica in addition to a consistency, Young's modulus, etc.
[0022] Especially Li2 O is a component effective [ sake / on an abrasion-proof disposition ] among R'2O. By this invention, 4% of the weight or more of Li2 O is contained in this viewpoint.
[0023] Although M2 O3 (one or more sorts as which M was chosen from B and aluminum) is not an indispensable component, it improves the chemistry endurance of glass by little addition, and can manufacture uniform glass. Glass is made to contain 0.1 % of the weight or more preferably. However, a consistency rises and, as a result, too much addition causes degradation of abrasion-proof nature.
[0024] Specifically, the desirable presentation range of the glass in this invention is essentially as follows.
[0025]
SiO2 74-78 Weight %, MgO 5-15 Weight %, CaO 0- 2 Weight %, ZnO 0- 2 Weight %, Li2 O 4-16 Weight %, Na2 O 0- 5 Weight %, K2 O 0- 7 Weight %, B-2 O3 0- 2 Weight %, aluminum 2O3 0- 2 Weight %.
[0026] It says that the above-mentioned principal component as used in the field of this invention which becomes "essential" from SiO2, M2 O3, RO, and R'2O occupies 96% of the weight or more of the whole glass. Fe, nickel, Se, Co, Ce, etc. can be added as a minor constituent to others for the purpose of control of homogenization of the whole glass, coloring, infrared penetrability, and ultraviolet-rays penetrability.
[0027] Moreover, in order to manufacture more homogeneous glass more easily, a well-known clarifier can also be added. There are SO3, Cl, etc. as this clarifier.
[0028] Since the glass of this invention is excellent also in melting nature, it can apply various kinds of manufacture approaches. That is, each raw material is prepared so that it may become a target system according to a conventional method, and this is heated and vitrified at 1450-1600 degrees C. Subsequently, after carrying out founding of this melting glass, it fabricates in a predetermined configuration. When fabricating to sheet glass in that case, the roll-out method, a float glass process, the pressing method, etc. are used. Moreover, when making it various container configurations, the pressing method and the Ayr blowing method are used. Moreover, when fabricating on a fiber, the approach of pulling out from the pinhole made from platinum is used. The glass fabricated in this way is annealed like usual glass, and serves as goods.
[0029] Since generating of a blemish cannot make the glass of this invention essential easily, it has high endurance, without processing special on a front face. Moreover, extensive application can be performed from excelling also in melting nature.
[0030] It is free to add functional film, such as thermal reflective film, to a front face and especially to perform physical or strengthening by the chemical technique. Moreover, if it sees from the field of an application, it can be used for various applications, such as an object for cars, an object for construction, an object for bottles, and an object for fibers.
[0031] The glass of this invention can be used as veneer glass, a glass laminate, and multiple glass. When considering as a glass laminate and multiple glass, it is good also as a glass laminate and multiple glass using the glass comrade by this invention, and good also as a glass laminate and multiple glass using the glass by this invention, and other glass.
[0032] In this invention, the brittleness index value B proposed by loans as an index of the brittleness (abrasion-proof nature) of glass was used (B. R.Lawn and D.B.Marshall, J.Am.Ceram.Soc., 62[7-8]347-350 (1979)). here — the brittleness index value B — Vickers hardness number Hv of an ingredient Fracture toughness value Kc from — a formula (1) defines.
[0033]
[Equation 1]

$$B = H_v / K_c \qquad (1)$$

[0034] The big problem at the time of applying the index of this brittleness to glass is the fracture toughness value Kc. It is hard to evaluate correctly. Then, as a result of examining some technique, this invention person found out that brittleness could be quantitatively evaluated from the relation between the magnitude of the marks of the indenter which remains in a glass front face, and the die length of the crack generated from the four corners of marks, when the Vickers indenter was pushed in.
[0035] The relation is defined by the formula (2). Here, P is the pushing load of the Vickers indenter, and 2a and 2c are the die length (overall length of two symmetrical cracks containing the marks of an indenter) of the crack generated from the diagonal length and four corners of the Vickers indentation, respectively, as shown in drawing 1 .
[0036]
[Equation 2]

$$c/a = 0.0056 B^{2/3} P^{1/6} \qquad (2)$$

[0037] If the dimension and formula (2) of the Vickers indentation which were driven into the front face of various glass are used, the brittleness of glass can be evaluated easily.
[0038] Drawing 2 shows the relation between the brittleness index value B measured in this way and the abrasion loss by sandblasting. As for the brittleness index value B and the abrasion loss by sandblasting, it turns out that it is in a very strong correlation and the brittleness index value has been the very good index of abrasion-proof nature.
[0039] At this invention, viscosity is 102 as an index of melting nature. The temperature used as a poise is adopted. It can be said that glass with which this becomes 1600 degrees C or less has good melting nature, and the glass manufacture by scorification is easy for it to the same extent as the conventional soda lime silica glass.
[0040] Since generating of a blemish cannot make the glass of this invention essential easily, it has high endurance, without processing special on a front face. Moreover, extensive application can be performed from excelling also in solubility.
[0041]
[Example] Viscosity is 102 as 12 kinds of glass presentations considered in Table 1 and Table 2 as the glass (Examples 1-8) and the example of a comparison (Examples 9-12) of this invention, the consistency of this glass, a brittleness index value, and a melting nature index value. A poise and 104 The temperature (degree C) used as a poise is shown. The presentation of a table is an analysis value by fluorescence X rays.
[0042] After supplying 200g of raw material fine particles of each presentation to the crucible made from platinum, the heating dissolution was carried out agitating in 1450-1650-degree-C atmospheric air for 4 hours. There is all solubility comparable as usual soda lime glass, and it checked that there was no problem on manufacture. The glass of each presentation which dissolved in homogeneity was slushed into the mold of carbon, and was fabricated and cooled on about 10cm square at the plate with a thickness of 5mm. After the obtained glass gave annealing in 490-570 degrees C and removed distortion, it carried out cutting polish and was made into the sample with a thickness of 4mm on 2cm square.
[0043] In order to remove the surface residual stress by polish further, from the point [ distortion ] temperature of angle glass, the sample which ground and took out the mirror plane was heated to the temperature on some (100 degrees C/hr), and was annealed after maintenance (3 hours) (60 degrees C/hr). In this way, the brittleness was measured where surface heat and processing distortion are removed completely.
[0044] The Vickers hardness test machine was used for measurement of brittleness. Brittleness was computed according to the pushing load of the die length of a crack, and the Vickers indenter which drives an indentation into a glass front face and is generated from the rectangular head of the indentation with this equipment using (aforementioned 1) and aforementioned (2) types.
[0045] The pushing load was made into 5kg pile, and measured brittleness about all examples. Moreover, about the consistency, it computed by the Archimedes method from the dry weight of a sample, and underwater weight. The last digit was rounded off and they could be 4 figures, after using the highly precise balance measurable to a microgram for measurement and calculating to 5 figures of significant figures.
[0046] For the glass which is in the presentation range of this invention from Table 1 and Table 2, a consistency is 2.470g/cc or less exceeding 2.410 altogether, and the brittleness index value b is 1/2 or less [ 6700m - ], and viscosity is 102. The temperature used as a poise is 1600 degrees C or less.
[0047] It is 102, although a consistency is 2.470g/cc or less and the brittleness index value B has become 1/2 or less [ 6600m - ] to it in the example of a comparison out of range (Example 9, Example 10). Difficulty has the temperature used as a poise in the dissolution and a moldability above 1600 degrees C. At the example of a comparison (Example 11, Example 12), it is 102. Although the temperature used as a poise is easy for the dissolution and shaping below 1600 degrees C, the consistency is over cc in 2.470g /, and in order that the brittleness index value B may exceed -1/2 6600m, the improvement of abrasion-proof nature is not found.
[0048] Moreover, it turns out that a brittleness index value also falls as a consistency and brittleness show good forward correlation in these examples and a consistency falls, namely, a blemish cannot be attached easily and has become.
[0049] Furthermore, when the crack initiation load (load which a crack will generate from the rectangular head of an indentation for the first time beyond the load if the load is increased gradually) when stuffing the Vickers indenter into the glass of Example 2 in which the lowest brittleness index value was shown was searched for, it became 900g pile. With usual soda lime glass, the crack initiation load searched for by the same approach is a 200g pile, and was able to raise the crack initiation load up to 4.5 times by improving brittleness. This is a very large advantage, when the key factor of a fall on the strength considers being based on the blemish generated on the front face after glass manufacture at the time of real use of glass.
[0050] that is, by using the glass of this presentation, the fall on the strength by the surface crack at the time of real use can be reduced, as a result, the life of goods is boiled markedly, and is developed, and the dependability can be improved sharply.
[0051]
[Table 1]

| | | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| 組成 | $SiO_2$ | 75.1 | 75.1 | 75.1 | 75.1 | 75.0 | 75.0 |
| | MgO | 9.4 | 9.4 | 10.4 | 11.4 | 13.4 | 14.4 |
| | CaO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | ZnO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $Li_2O$ | 15.5 | 14.5 | 13.5 | 6.5 | 5.5 | 5.0 |
| | $Na_2O$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $K_2O$ | 0.0 | 0.0 | 0.0 | 6.0 | 5.0 | 4.5 |
| | $Al_2O_3$ | 0.0 | 1.0 | 1.0 | 1.0 | 1.1 | 1.1 |
| $RO+R_2O$ | | 24.9 | 23.9 | 23.9 | 23.9 | 23.9 | 23.9 |
| $RO/R_2O$ | | 0.61 | 0.65 | 0.77 | 0.91 | 1.28 | 1.52 |
| 密度(g/cc) | | 2.424 | 2.422 | 2.426 | 2.426 | 2.433 | 2.437 |
| B $(m^{-1/2})$ | | 6200 | 6100 | 6300 | 6300 | 6300 | 6400 |
| $10^2$poise (℃) | | 1264 | 1288 | 1288 | 1352 | 1356 | 1358 |
| $10^4$poise (℃) | | 826 | 851 | 864 | 951 | 966 | 974 |

[0052]
[Table 2]

| | | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|
| 組成 | $SiO_2$ | 77.0 | 77.9 | 80.3 | 83.0 | 58.9 | 67.0 |
| | MgO | 14.1 | 9.5 | 0.0 | 3.3 | 0.0 | 0.0 |
| | CaO | 0.0 | 1.0 | 9.4 | 0.0 | 4.8 | 10.0 |
| | ZnO | 0.0 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $Li_2O$ | 5.0 | 10.6 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $Na_2O$ | 1.1 | 0.0 | 10.3 | 10.3 | 16.1 | 15.0 |
| | $K_2O$ | 2.8 | 0.0 | 0.0 | 0.0 | 0.0 | 5.0 |
| | $Al_2O_3$ | 0.0 | 0.0 | 0.0 | 3.4 | 20.2 | 3.0 |
| $RO+R_2O$ | | 23.0 | 22.1 | 19.7 | 13.6 | 20.9 | 30.0 |
| $RO/R_2O$ | | 1.58 | 1.09 | 0.91 | 0.32 | 0.30 | 0.50 |
| 密度(g/cc) | | 2.430 | 2.430 | 2.431 | 2.347 | 2.488 | 2.522 |
| B $(m^{-1/2})$ | | 6300 | 6300 | 6100 | 4000 | 6800 | 7000 |
| $10^2$poise (℃) | | 1390 | 1450 | 1786 | 2314 | 1338 | 1387 |
| $10^4$poise (℃) | | 1033 | 985 | 1179 | 1366 | 976 | 1066 |

[0053]
[Effect of the Invention] by using this, it can reduce the fall on the strength by the surface crack at the time of real use, as a result, the glass of this invention boils the life of goods markedly, and develops it, and can improve the dependability sharply while being able to manufacture it with sufficient productivity with scorification.

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to glass with very high abrasion-proof nature.

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[Translation done.]

PRIOR ART

[Description of the Prior Art] Glass is essentially a weak ingredient, and if the reinforcement falls and the force is added there by the minute surface crack generated especially at the time of use, the crack which makes a minute blemish the start will extend and it will result in destruction.
[0003] Therefore, in order to raise the endurance of glass, the attempt which a blemish tends to make it hard to be attached to a front face is performed for many years. For example, it is surface hard coating, and is surface strengthening by the ion exchange, and is physical strengthening by quenching.
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[0009] After all, conventionally, there was only recognition of extent that abrasion-proof nature falls as quartz glass is most excellent in abrasion-proof nature and network modifiers increased in number about the relation between the ease of attaching of the blemish on the front face of glass, and a presentation.

[Translation done.]

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EFFECT OF THE INVENTION

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[Effect of the Invention] by using this, it can reduce the fall on the strength by the surface crack at the time of real use, as a result, the glass of this invention boils the life of goods markedly, and develops it, and can improve the dependability sharply while being able to manufacture it with sufficient productivity with scorification.

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[Translation done.]

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] Based on the conventional recognition, it is SiO2 in order to raise a degree of hardness simply. If it is made to increase, since it will be hard coming to dissolve, production by scorification with sufficient productivity becomes difficult. On the other hand, in the glass of a soda lime silica system, generally, when production with scorification chooses an easy presentation, the improvement in a degree of hardness has so much the problem that it does not see.
[0011] Moreover, by performing a certain processing on the surface of glass, in the approach of conquering brittleness, the after treatment after glass shaping is required, and there are a problem of a rise of cost, a problem of a limit of application, a problem that the effectiveness does not maintain at the time of use depending on the case.
[0012] Production by scorification is possible for it, and the purpose of this invention is to offer the glass which maintained fundamentally the advantages, such as endurance which soda lime glass has, while it improves the not above-mentioned problem that the conventional technique has, i.e., reforming of after treatment or a front face, but the brittleness of glass itself and prevents generating of the blemish by the external force at the time of real use.

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[Translation done.]

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MEANS

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[Means for Solving the Problem] this invention — essential — 74 – 78% of the weight of SiO2, and RO/R' — 15 – 30% of the weight of RO+R'2O (R — Mg —) whose 2O ratios are 0.6–1.6 One or more sorts and R' which were chosen from calcium and Zn One or more sorts chosen from Li, Na, and K, It is abrasion-proof nature glass characterized by consisting of 4% of the weight or more of Li2 O, and 0 – 10% of the weight of M2 O3 (one or more sorts as which M was chosen from B and aluminum), and carrying out a consistency in 2.47g/cc or less exceeding 2.41g/cc.
[0014] this invention person considers the presentation and the relation of abrasion-proof nature in a detail about various soda lime silica glass, and sets to glass presentation within the limits of the result above-mentioned. By carrying out the consistency exceeding 2.41g/cc in 2.47g/cc or less (the consistency of the usual soda lime silica glass being about 2.49–2.52g/cc) While maintaining fundamentally properties, such as melting nature in the conventional soda lime silica glass, and chemical durability, it found out that it was hard coming to attach a blemish very compared with the conventional soda lime silica glass.
[0015] When the consistency of glass was especially lowered from cc in 2.52g /by the above-mentioned presentation and it became [ cc ] in 2.47g /or less, it found out that abrasion-proof nature improved rapidly to other properties changing gradually. In a presentation region with a this of about 2.47g [/cc ], i.e., consistency, it thinks for the flexibility (degree of freedom of the bond angle in atomic level) of glass structure to change rapidly.
[0016] That is, it is based on having found out that this invention was possible to presentation within the limits which whose consistency is the factor which influences abrasion-proof nature most in soda lime silica glass, and has the control. And if the presentation is optimized as shown in the after-mentioned example, the glass whose actual reinforcement the generating load of a blemish was very high and also improved greatly compared with the usual soda lime silica glass will be obtained easily [ manufacture by scorification ].
[0017] Next, the presentation range of the glass of this invention is explained.
[0018] SiO2 It is the principal component which forms the network structure of glass. Since a consistency rises and crack propagation becomes easy while the amount of non-bridging oxygen will increase relatively and the network structure will become weak, if there is too little this, the reinforcement itself becomes low. Moreover, if many [ too ], melting nature will worsen and it will become difficult to obtain homogeneous glass with scorification. By this invention, it may be 74 – 78 % of the weight to the whole glass in this viewpoint.
[0019] R'2O (one or more sorts as which R' was chosen from Li, Na, and K) is a component indispensable to a soluble improvement with RO (one or more sorts as which R was chosen from Mg, calcium, and Zn) indispensable to a soluble improvement and an improvement of chemical durability. The amount of R'2O and RO is made into 15 – 30 % of the weight with a total amount.
[0020] By carrying out constant-rate content of the RO, the chemical endurance of the whole glass is improvable. In this viewpoint, weight ratio RO/R'2O is set to 0.6–1.6 by this invention.
[0021] Such R to add and R' Small [ an element number ] as a general trend, a light element is effective in reduction of a consistency, and abrasion-proof nature is also improved as a result. It is desirable to make [ many ] Mg as R rather than calcium in this viewpoint. However, there are some which also show different behavior under the effect of the element added by coincidence in some elements. These are considered because there are a form of the network structure where the factor which determines abrasion-proof nature makes a subject the amount of non-bridging oxygen and a silica in addition to a consistency, Young's modulus, etc.
[0022] Especially Li2 O is a component effective [ sake / on an abrasion-proof disposition ] among R'2O. By this invention, 4% of the weight or more of Li2 O is contained in this viewpoint.
[0023] Although M2 O3 (one or more sorts as which M was chosen from B and aluminum) is not an indispensable component, it improves the chemistry endurance of glass by little addition, and can manufacture uniform glass. Glass is made to contain 0.1 % of the weight or more preferably. However, a consistency rises and, as a result, too much addition causes degradation of abrasion-proof nature.
[0024] Specifically, the desirable presentation range of the glass in this invention is essentially as follows.
[0025]
SiO2 74–78 Weight %, MgO 5–15 Weight %, CaO 0– 2 Weight %, ZnO 0– 2 Weight %, Li2 O 4–16 Weight %, Na2 O 0– 5 Weight %, K2 O 0– 7 Weight %, B–2 O3 0– 2 Weight %, aluminum 2O3 0– 2 Weight %.
[0026] It says that the above-mentioned principal component as used in the field of this invention which becomes "essential" from SiO2, M2 O3, RO, and R'2O occupies 96% of the weight or more of the whole glass. Fe, nickel, Se, Co, Ce, etc. can be added as a minor constituent to others for the purpose of control of homogenization of the whole glass, coloring, infrared penetrability, and ultraviolet-rays penetrability.
[0027] Moreover, in order to manufacture more homogeneous glass more easily, a well-known clarifier can also be added. There are SO3, Cl, etc. as this clarifier.
[0028] Since the glass of this invention is excellent also in melting nature, it can apply various kinds of manufacture approaches. That is, each raw material is prepared so that it may become a target system according to a conventional method, and this is heated and vitrified at 1450–1600 degrees C. Subsequently, after carrying out founding of this melting glass, it fabricates in a predetermined configuration. When fabricating to sheet glass in that case, the roll-out method, a float glass process, the pressing method, etc. are used. Moreover, when making it various container configurations, the pressing method and the Ayr blowing method are used. Moreover, when fabricating on a fiber, the approach of pulling out from the pinhole made from platinum is used. The glass

fabricated in this way is annealed like usual glass, and serves as goods.
[0029] Since generating of a blemish cannot make the glass of this invention essential easily, it has high endurance, without processing special on a front face. Moreover, extensive application can be performed from excelling also in melting nature.
[0030] It is free to add functional film, such as thermal reflective film, to a front face and especially to perform physical or strengthening by the chemical technique. Moreover, if it sees from the field of an application, it can be used for various applications, such as an object for cars, an object for construction, an object for bottles, and an object for fibers.
[0031] The glass of this invention can be used as veneer glass, a glass laminate, and multiple glass. When considering as a glass laminate and multiple glass, it is good also as a glass laminate and multiple glass using the glass comrade by this invention, and good also as a glass laminate and multiple glass using the glass by this invention, and other glass.
[0032] In this invention, the brittleness index value B proposed by loans as an index of the brittleness (abrasion-proof nature) of glass was used (B. R.Lawn and D.B.Marshall, J.Am.Ceram.Soc., 62[7-8]347-350 (1979)). here -- the brittleness index value B -- Vickers hardness number Hv of an ingredient Fracture toughness value Kc from -- a formula (1) defines.
[0033]
[Equation 1]

$$B = H_v / K_c \qquad (1)$$

[0034] The big problem at the time of applying the index of this brittleness to glass is the fracture toughness value Kc. It is hard to evaluate correctly. Then, as a result of examining some technique, this invention person found out that brittleness could be quantitatively evaluated from the relation between the magnitude of the marks of the indenter which remains in a glass front face, and the die length of the crack generated from the four corners of marks, when the Vickers indenter was pushed in.
[0035] The relation is defined by the formula (2). Here, P is the pushing load of the Vickers indenter, and 2a and 2c are the die length (overall length of two symmetrical cracks containing the marks of an indenter) of the crack generated from the diagonal length and four corners of the Vickers indentation, respectively, as shown in drawing 1 .
[0036]
[Equation 2]

$$c/a = 0.0056 B^{2/3} P^{1/6} \qquad (2)$$

[0037] If the dimension and formula (2) of the Vickers indentation which were driven into the front face of various glass are used, the brittleness of glass can be evaluated easily.
[0038] Drawing 2 shows the relation between the brittleness index value B measured in this way and the abrasion loss by sandblasting. As for the brittleness index value B and the abrasion loss by sandblasting, it turns out that it is in a very strong correlation and the brittleness index value has been the very good index of abrasion-proof nature.
[0039] At this invention, viscosity is 102 as an index of melting nature. The temperature used as a poise is adopted. It can be said that glass with which this becomes 1600 degrees C or less has good melting nature, and the glass manufacture by scorification is easy for it to the same extent as the conventional soda lime silica glass.
[0040] Since generating of a blemish cannot make the glass of this invention essential easily, it has high endurance, without processing special on a front face. Moreover, extensive application can be performed from excelling also in solubility.

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[Translation done.]

EXAMPLE

[Example] Viscosity is 102 as 12 kinds of glass presentations considered in Table 1 and Table 2 as the glass (Examples 1-8) and the example of a comparison (Examples 9-12) of this invention, the consistency of this glass, a brittleness index value, and a melting nature index value. A poise and 104 The temperature (degree C) used as a poise is shown. The presentation of a table is an analysis value by fluorescence X rays.
[0042] After supplying 200g of raw material fine particles of each presentation to the crucible made from platinum, the heating dissolution was carried out agitating in 1450-1650-degree-C atmospheric air for 4 hours. There is all solubility comparable as usual soda lime glass, and it checked that there was no problem on manufacture. The glass of each presentation which dissolved in homogeneity was slushed into the mold of carbon, and was fabricated and cooled on about 10cm square at the plate with a thickness of 5mm. After the obtained glass gave annealing in 490-570 degrees C and removed distortion, it carried out cutting polish and was made into the sample with a thickness of 4mm on 2cm square.
[0043] In order to remove the surface residual stress by polish further, from the point [ distortion ] temperature of angle glass, the sample which ground and took out the mirror plane was heated to the temperature on some (100 degrees C/hr), and was annealed after maintenance (3 hours) (60 degrees C/hr). In this way, the brittleness was measured where surface heat and processing distortion are removed completely.
[0044] The Vickers hardness test machine was used for measurement of brittleness. Brittleness was computed according to the pushing load of the die length of a crack, and the Vickers indenter which drives an indentation into a glass front face and is generated from the rectangular head of the indentation with this equipment using (aforementioned 1) and aforementioned (2) types.
[0045] The pushing load was made into 5kg pile, and measured brittleness about all examples. Moreover, about the consistency, it computed by the Archimedes method from the dry weight of a sample, and underwater weight. The last digit was rounded off and they could be 4 figures, after using the highly precise balance measurable to a microgram for measurement and calculating to 5 figures of significant figures.
[0046] For the glass which is in the presentation range of this invention from Table 1 and Table 2, a consistency is 2.470g/cc or less exceeding 2.410 altogether, and the brittleness index value b is 1/2 or less [ 6700m - ], and viscosity is 102. The temperature used as a poise is 1600 degrees C or less.
[0047] It is 102, although a consistency is 2.470g/cc or less and the brittleness index value B has become 1/2 or less [ 6600m - ] to it in the example of a comparison out of range (Example 9, Example 10). Difficulty has the temperature used as a poise in the dissolution and a moldability above 1600 degrees C. At the example of a comparison (Example 11, Example 12), it is 102. Although the temperature used as a poise is easy for the dissolution and shaping below 1600 degrees C, the consistency is over cc in 2.470g /, and in order that the brittleness index value B may exceed -1/2 6600m, the improvement of abrasion-proof nature is not found.
[0048] Moreover, it turns out that a brittleness index value also falls as a consistency and brittleness show good forward correlation in these examples and a consistency falls, namely, a blemish cannot be attached easily and has become.
[0049] Furthermore, when the crack initiation load (load which a crack will generate from the rectangular head of an indentation for the first time beyond the load if the load is increased gradually) when stuffing the Vickers indenter into the glass of Example 2 in which the lowest brittleness index value was shown was searched for, it became 900g pile. With usual soda lime glass, the crack initiation load searched for by the same approach is a 200g pile, and was able to raise the crack initiation load up to 4.5 times by improving brittleness. This is a very large advantage, when the key factor of a fall on the strength considers being based on the blemish generated on the front face after glass manufacture at the time of real use of glass.
[0050] that is, by using the glass of this presentation, the fall on the strength by the surface crack at the time of real use can be reduced, as a result, the life of goods is boiled markedly, and is developed, and the dependability can be improved sharply.
[0051]
[Table 1]

| | | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| 組成 | $SiO_2$ | 75.1 | 75.1 | 75.1 | 75.1 | 75.0 | 75.0 |
| | MgO | 9.4 | 9.4 | 10.4 | 11.4 | 13.4 | 14.4 |
| | CaO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | ZnO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $Li_2O$ | 15.5 | 14.5 | 13.5 | 6.5 | 5.5 | 5.0 |
| | $Na_2O$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $K_2O$ | 0.0 | 0.0 | 0.0 | 6.0 | 5.0 | 4.5 |
| | $Al_2O_3$ | 0.0 | 1.0 | 1.0 | 1.0 | 1.1 | 1.1 |
| $RO+R_2O$ | | 24.9 | 23.9 | 23.9 | 23.9 | 23.9 | 23.9 |
| $RO/R_2O$ | | 0.61 | 0.65 | 0.77 | 0.91 | 1.28 | 1.52 |
| 密度(g/cc) | | 2.424 | 2.422 | 2.426 | 2.426 | 2.433 | 2.437 |
| B $(m^{-1/2})$ | | 6200 | 6100 | 6300 | 6300 | 6300 | 6400 |
| $10^3$poise (℃) | | 1264 | 1288 | 1288 | 1352 | 1356 | 1358 |
| $10^4$poise (℃) | | 826 | 851 | 864 | 951 | 966 | 974 |

[0052]
[Table 2]

| | | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|
| 組成 | $SiO_2$ | 77.0 | 77.9 | 80.3 | 83.0 | 58.9 | 67.0 |
| | MgO | 14.1 | 9.5 | 0.0 | 3.3 | 0.0 | 0.0 |
| | CaO | 0.0 | 1.0 | 9.4 | 0.0 | 4.8 | 10.0 |
| | ZnO | 0.0 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $Li_2O$ | 5.0 | 10.6 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $Na_2O$ | 1.1 | 0.0 | 10.3 | 10.3 | 16.1 | 15.0 |
| | $K_2O$ | 2.8 | 0.0 | 0.0 | 0.0 | 0.0 | 5.0 |
| | $Al_2O_3$ | 0.0 | 0.0 | 0.0 | 3.4 | 20.2 | 3.0 |
| $RO+R_2O$ | | 23.0 | 22.1 | 19.7 | 13.6 | 20.9 | 30.0 |
| $RO/R_2O$ | | 1.58 | 1.09 | 0.91 | 0.32 | 0.30 | 0.50 |
| 密度(g/cc) | | 2.430 | 2.430 | 2.431 | 2.347 | 2.488 | 2.522 |
| B $(m^{-1/2})$ | | 6300 | 6300 | 6100 | 4000 | 6800 | 7000 |
| $10^3$poise (℃) | | 1390 | 1450 | 1786 | 2314 | 1338 | 1387 |
| $10^4$poise (℃) | | 1033 | 985 | 1179 | 1366 | 976 | 1066 |

[Translation done.]

* NOTICES *



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3.In the drawings, any words are not translated.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]
[Drawing 1] The explanatory view explaining the definition of the brittleness in this invention
[Drawing 2] The graph which shows the relation between the brittleness index value B and the abrasion loss by sandblasting

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[Translation done.]

* NOTICES *



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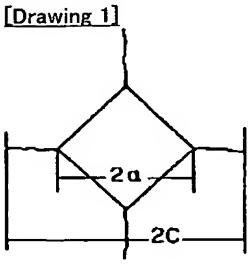
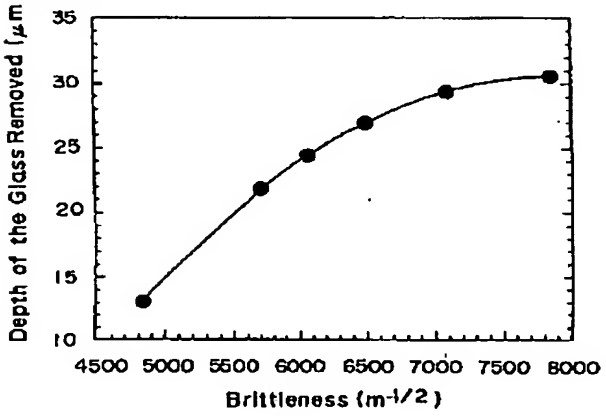
DRAWINGS

[Drawing 1]




[Drawing 2]

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(19)日本国特許庁（ＪＰ）　(12) **公開特許公報（Ａ）**　(11)特許出願公開番号

**特開平9－52729**

(43)公開日　平成９年(1997)２月25日

| (51)Int.Cl.[6] | | 識別記号 | 庁内整理番号 | ＦＩ | | 技術表示箇所 |
|---|---|---|---|---|---|---|
| Ｃ０３Ｃ | 3/078 | | | Ｃ０３Ｃ | 3/078 | |
| | 3/087 | | | | 3/087 | |
| | 3/089 | | | | 3/089 | |
| | 3/091 | | | | 3/091 | |
| | 3/093 | | | | 3/093 | |

審査請求　未請求　請求項の数４　ＯＬ　（全 ６ 頁）　最終頁に続く

(21)出願番号　特願平8－146256

(22)出願日　平成８年(1996)６月７日

(31)優先権主張番号　特願平7－143472

(32)優先日　平７(1995)６月９日

(33)優先権主張国　日本（ＪＰ）

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(54)【発明の名称】　耐擦傷性ガラス

(57)【要約】
【課題】きわめて耐擦傷性の高いガラスを得る。
【解決手段】本質的に７４～７８重量%のＳｉＯ$_2$、重量比ＲＯ／Ｒ'$_2$Ｏ比が０．６～１．６であるところの１５～３０重量%のＲＯ＋Ｒ'$_2$Ｏ、４重量%以上のＬｉ$_2$Ｏ、０～１０重量%のＭ$_2$Ｏ$_3$（ＭはＢおよび／またはＡｌ）からなり、密度が２．４１ｇ／ｃｃを超えて２．４７ｇ／ｃｃ以下とされることを特徴とする。

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【特許請求の範囲】

【請求項１】本質的に７４～７８重量%のＳｉＯ₂、ＲＯ／Ｒ'₂Ｏ重量比が０．６～１．６であるところの１５～３０重量%のＲＯ＋Ｒ'₂Ｏ（ＲはＭｇ、ＣａおよびＺｎから選ばれた１種以上、Ｒ'はＬｉ、ＮａおよびＫから選ばれた１種以上）、４重量%以上のＬｉ₂Ｏ、０～１０重量%のＭ₂Ｏ₃（ＭはＢおよびＡｌから選ばれた１種以上）からなり、密度が２．４１ｇ／ｃｃを超えて２．４７ｇ／ｃｃ以下とされることを特徴とする耐擦傷性ガラス。

【請求項２】脆さ指標値Ｂが６７００$m^{-1/2}$以下であることを特徴とする請求項１記載の耐擦傷性ガラス。ここで、Ｂ＝Ｈᵥ／Ｋ꜀（Ｈᵥはビッカース硬さ、Ｋ꜀は破壊靭性値）である。

【請求項３】粘度が$10^2$ポイズとなる温度が１６００℃以下であることを特徴とする請求項１または２記載の耐擦傷性ガラス。

【請求項４】本質的に、以下の成分からなる請求項１、２または３記載の耐擦傷性ガラス。

| | | |
|---|---|---|
| ＳｉＯ₂ | ７４～７８ | 重量%、 |
| ＭｇＯ | ５～１５ | 重量%、 |
| ＣａＯ | ０～　２ | 重量%、 |
| ＺｎＯ | ０～　２ | 重量%、 |
| Ｌｉ₂Ｏ | ４～１６ | 重量%、 |
| Ｎａ₂Ｏ | ０～　５ | 重量%、 |
| Ｋ₂Ｏ | ０～　７ | 重量%、 |
| Ｂ₂Ｏ₃ | ０～　２ | 重量%、 |
| Ａｌ₂Ｏ₃ | ０～　２ | 重量%。 |

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、耐擦傷性がきわめて高いガラスに関する。

【０００２】

【従来の技術】ガラスは本質的に脆い材料であり、特に使用時に発生する微小な表面傷によってその強度が低下し、そこに力が加わると、微小傷を端緒とするクラックが伸展して破壊に至る。

【０００３】したがって、ガラスの耐久性を上げるために、表面に傷が付きにくくしようとする試みは古くから行われている。たとえばそれは表面のハードコーティングであり、イオン交換による表面強化であり、また急冷による物理強化である。

【０００４】これらの技術はガラスの表面を他の材料で覆って傷の発生を防ぐ方法と、表面に圧縮残留応力を発生させて傷の発生、伸展を防ぐ方法に大別され、どちらにせよ、本質的にガラスそのものの脆さを改善する試みではない。したがって、表面のコーティングが磨耗、劣化などにより除去されてしまったり、あるいは温度の上昇などによって表面の残留応力が消失してしまう環境下においてその効果は発現されないという問題がある。

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【０００５】一方、現在もっとも汎用されているソーダライムシリカガラスは歴史的にも推移があるが、一般的には以下のような組成を有する。

【０００６】

| | | |
|---|---|---|
| ＳｉＯ₂ | ６６～７５ | 重量%、 |
| ＭｇＯ | ０～　５ | 重量%、 |
| ＣａＯ | ７～１２ | 重量%、 |
| Ｎａ₂Ｏ | １２～２０ | 重量%、 |
| Ｋ₂Ｏ | ０～　３ | 重量%、 |
| Ａｌ₂Ｏ₃ | ０～　４ | 重量%。 |

【０００７】ソーダライムシリカガラスにおいて、組成と硬度との関係については、研究は多くない。一般的な認識としては、ＳｉＯ₂を増加させると強度が上がること、ＣａＯでＮａ₂Ｏを置換するとネットワークの結合性が上がり、強度が向上すること、Ａｌ₂Ｏ₃の添加が強度および硬度の向上に役立つこと、などがある程度である。

【０００８】さらに表面の傷のつきやすさに対応する擦傷硬度については、実際のガラスの強度を決定するうえで重要であるが、ガラスの研磨現象は複雑で、必ずしもビッカース硬度との相関性が良くない。これは、耐擦傷性が、硬度に関係する因子のみならず微細クラックの発生と伸展による試料からの脱離、摩擦熱による影響があるためと考えられる。

【０００９】結局、従来は、ガラス表面の傷のつきやすさと組成との関係については、石英ガラスが最も耐擦傷性に優れており、網目修飾イオンが増えるにしたがい、耐擦傷性が低下するという程度の認識しかなかった。

【００１０】

【発明が解決しようとする課題】従来の認識に基づき、単純に硬度を上げるためにＳｉＯ₂を増加させると、溶解しにくくなるため、生産性の良い溶融法による生産が困難になる。一方、ソーダライムシリカ系のガラスにおいて、一般的には、溶融法での生産が容易な組成を選択すると、さほど硬度の向上は見られないという問題がある。

【００１１】また、ガラスの表面に何らかの処理を行うことによって脆さを克服する方法においては、ガラス成形後の後処理が必要であり、コストの上昇の問題や適用の制限の問題、場合によっては使用時にその効果が持続しない問題などがある。

【００１２】本発明の目的は、従来技術が有する前述の問題、すなわち、後処理や表面の改質ではなく、ガラスそのものの脆さを改善し、実使用時の外力による傷の発生を防ぐとともに、溶融法による生産が可能でソーダライムガラスの持つ耐久性などの長所を基本的に維持したガラスを提供することにある。

【００１３】

【課題を解決するための手段】本発明は、本質的に７４～７８重量%のＳｉＯ₂、ＲＯ／Ｒ'₂Ｏ比が０．６～

１．６であるところの１５～３０重量%のＲＯ＋Ｒ'₂Ｏ（ＲはＭｇ、ＣａおよびＺｎから選ばれた１種以上、Ｒ'はＬｉ、ＮａおよびＫから選ばれた１種以上）、４重量%以上のＬｉ₂Ｏ、０～１０重量%のＭ₂Ｏ₃（ＭはＢおよびＡｌから選ばれた１種以上）からなり、密度が２．４１ｇ／ｃｃを超えて２．４７ｇ／ｃｃ以下とされることを特徴とする耐擦傷性ガラスである。

【００１４】本発明者は、多種のソーダライムシリカガラスについてその組成と耐擦傷性の関係を詳細に検討し、その結果前述のガラス組成範囲内において、その密度を２．４１ｇ／ｃｃを超えて２．４７ｇ／ｃｃ以下（通常のソーダライムシリカガラスの密度は２．４９～２．５２ｇ／ｃｃ程度）とすることによって、従来のソーダライムシリカガラスにおける溶融性、化学的耐久性などの特性を基本的に維持するとともに、従来のソーダライムシリカガラスに比べて大変に傷がつきにくくなることを見いだした。

【００１５】特に、前述の組成でガラスの密度を２．５２ｇ／ｃｃから下げていった場合に２．４７ｇ／ｃｃ以下になると、他の特性は徐々に変化するのに対して、耐擦傷性は急激に改善されることを見いだした。これはすなわち、密度２．４７ｇ／ｃｃ近傍の組成域において、ガラス構造の柔軟性（原子レベルでの結合角の自由度）が急激に変わるためと考えられる。

【００１６】すなわち、本発明はソーダライムシリカガラスにおいて、密度が最も耐擦傷性に影響する因子であり、また、その制御がある組成範囲内において可能であることを見いだしたことに基づく。そして、後記実施例に示すとおり、その組成を最適化すれば、溶融法による製造が容易で、かつ、通常のソーダライムシリカガラスに比べて傷の発生荷重が非常に高く、実際の強度も大きく向上したガラスが得られる。

【００１７】次に本発明のガラスの組成範囲について説明する。

【００１８】ＳｉＯ₂はガラスの網目構造を形成する主成分である。これが少なすぎると、相対的に非架橋酸素量が増えて、網目構造が弱くなるとともに、密度が上昇してクラック伝播が容易となるため、強度自体が低くなる。また、多すぎると、溶融性が悪くなり、溶融法によって均質なガラスを得ることが困難となる。この観点で本発明では、ガラス全体に対して７４～７８重量%とする。

【００１９】Ｒ'₂Ｏ（Ｒ'はＬｉ、ＮａおよびＫから選ばれた１種以上）は溶解性の改善に必須であり、また、ＲＯ（ＲはＭｇ、ＣａおよびＺｎから選ばれた１種以上）は溶解性の改善および化学的耐久性の改善に必須な成分である。Ｒ'₂ＯとＲＯの量は合量で１５～３０重量%とする。

【００２０】ＲＯを一定量含有することにより、ガラス全体の化学的な耐久性を改善することができる。この観点で、本発明では、重量比ＲＯ／Ｒ'₂Ｏは、０．６～１．６とされる。



【００２１】添加するこれらのＲ、Ｒ'は、傾向としては元素番号の小さい、すなわち軽い元素が密度の低減に有効であり、結果として耐擦傷性も改善される。かかる観点で、Ｒとしては、Ｃａよりはむしろ Ｍｇを多くすることが好ましい。ただし、いくつかの元素においては同時に添加される元素の影響により、異なった挙動も示すものもある。これらは耐擦傷性を決定する因子が密度以外に非架橋酸素量やシリカを主体とする網目構造の形、ヤング率などがあるためと考えられる。

【００２２】Ｒ'₂Ｏのうち特にＬｉ₂Ｏは、耐擦傷性向上のために有効な成分である。本発明では、この観点で４重量%以上のＬｉ₂Ｏを含有する。

【００２３】Ｍ₂Ｏ₃（ＭはＢおよびＡｌから選ばれた１種以上）は必須成分ではないが、少量の添加によりガラスの化学耐久性を向上して、均一なガラスを製造できる。好ましくは０．１重量%以上をガラスに含有させる。ただし、過度の添加は、密度が上昇し、その結果耐擦傷性の劣化を引き起こす。

【００２４】具体的には、本発明におけるガラスの好ましい組成範囲は、本質的に以下のようになる。

【００２５】

| | | |
|---|---|---|
| ＳｉＯ₂ | ７４～７８ | 重量%、 |
| ＭｇＯ | ５～１５ | 重量%、 |
| ＣａＯ | ０～　２ | 重量%、 |
| ＺｎＯ | ０～　２ | 重量%、 |
| Ｌｉ₂Ｏ | ４～１６ | 重量%、 |
| Ｎａ₂Ｏ | ０～　５ | 重量%、 |
| Ｋ₂Ｏ | ０～　７ | 重量%、 |
| Ｂ₂Ｏ₃ | ０～　２ | 重量%、 |
| Ａｌ₂Ｏ₃ | ０～　２ | 重量%。 |

【００２６】本発明でいう、「本質的」とは、ＳｉＯ₂、Ｍ₂Ｏ₃、ＲＯ、およびＲ'₂Ｏからなる上記の主成分がガラス全体の９６重量%以上を占めることをいう。他に微量成分として、ガラス全体の均質化、着色、赤外線透過能および紫外線透過能の制御の目的で、Ｆｅ、Ｎｉ、Ｓｅ、Ｃｏ、Ｃｅなどを添加できる。

【００２７】また、より均質なガラスをより容易に製造するために、公知の清澄剤も添加できる。かかる清澄剤としては、ＳＯ₃、Ｃｌなどがある。

【００２８】本発明のガラスは、溶融性にも優れるため、各種の製造方法が適用できる。すなわち、常法にしたがって目標組成になるように各原料を調合し、これを１４５０～１６００℃に加熱してガラス化する。次いでこの溶融ガラスを清澄した後、所定の形状に成形する。その際、板ガラスに成形する場合は、ロールアウト法、フロート法、プレス法等が使用される。また、各種容器形状にする場合にはプレス法、エアーブロウ法が使用される。また、ファイバに成形する場合には、白金製のビ

ンホールから引き出す方法が使用される。かくして成形されたガラスは通常のガラスと同様に徐冷され、商品となる。

【００２９】本発明のガラスは本質的に傷の発生がしにくいため、表面に特段の処理を施すことなく高い耐久性を有する。また、溶融性にも優れることから、広範な応用ができる。

【００３０】特に、熱性反射膜等の機能性膜を表面に付加すること、物理的または化学的手法による強化などを行うことは自由である。また、用途の面からみれば、車両用、建築用、びん用、ファイバ用など、種々の用途に使用できる。

【００３１】本発明のガラスは、単板ガラス、合わせガラス、複層ガラスとして使用できる。合わせガラス、複層ガラスとする場合は、本発明によるガラス同志を使用して合わせガラス、複層ガラスとしてもよく、本発明によるガラスと他のガラスとを使用し合わせガラス、複層ガラスとしてもよい。

【００３２】本発明において、ガラスの脆さ（耐擦傷性）の指標としてはローンらによって提案された脆さ指標値Ｂを使用した（B.R.Lawn and D.B.Marshall,J.Am.Ceram.Soc.,62[7-8]347-350(1979)）。ここで、脆さ指標値Ｂは材料のビッカース硬さ$H_v$と破壊靭性値$K_c$から式（１）により定義される。

【００３３】

【数１】

$$B=H_v/K_c \qquad (1)$$

【００３４】この脆さの指標をガラスに適用する際の大きな問題は破壊靭性値$K_c$が正確に評価しにくいことである。そこで、本発明者は、いくつかの手法を検討した結果、ビッカース圧子を押し込んだときにガラス表面に残る圧子の痕の大きさと痕の四隅から発生するクラックの長さとの関係から脆さを定量的に評価できることを見いだした。

【００３５】その関係は式（２）により定義される。ここで、Ｐはビッカース圧子の押し込み荷重であり、２ａ、２ｃはそれぞれ、図１に示したように、ビッカース圧痕の対角長および四隅から発生するクラックの長さ（圧子の痕を含む対称な２つのクラックの全長）である。

【００３６】

【数２】

$$c/a=0.0056B^{2/3}P^{1/6} \qquad (2)$$

【００３７】各種ガラスの表面に打ち込んだビッカース圧痕の寸法と式（２）を用いれば、ガラスの脆さを簡単に評価できる。

【００３８】図２は、こうして測定した脆さ指標値Ｂとサンドブラストによる摩耗量との関係を示す。脆さ指標値Ｂと、サンドブラストによる摩耗量とは非常に強い相関関係にあり、脆さ指標値が耐擦傷性の大変良い指標になっていることがわかる。

【００３９】本発明では、溶融性の指標として、粘度が$10^2$ポイズとなる温度を採用する。これが１６００℃以下となるようなガラスは従来のソーダライムシリカガラスと同程度に溶融性が良く、溶融法によるガラス製造が容易であるといえる。

【００４０】本発明のガラスは本質的に傷の発生がしにくいため、表面に特段の処理を施すことなく高い耐久性を有する。また、溶解性にも優れることから、広範な応用ができる。

【００４１】

【実施例】表１、表２には本発明のガラス（例１～８）および比較例（例９～１２）として検討した１２種類のガラス組成、同ガラスの密度、脆さ指標値および溶融性指標値として、粘度が$10^2$ポイズ、$10^4$ポイズとなる温度（℃）を示す。表の組成は、蛍光Ｘ線による分析値である。

【００４２】各組成の原料粉体２００ｇを白金製の坩堝に投入した後、１４５０～１６５０℃大気中にて４時間撹拌しながら加熱溶解した。すべて通常のソーダライムガラスと同程度の溶解性があり、製造上の問題がないことを確認した。均一に溶解した各組成のガラスは、カーボンの型に流し込んで約１０ｃｍ角で厚さ５ｍｍの板に成形・冷却した。得られたガラスは４９０～５７０℃においてアニールを施し歪みを除去した後、切断研磨し、２ｃｍ角で厚さ４ｍｍの試料とした。

【００４３】研磨して鏡面を出した試料はさらに研磨による表面残留応力を除去するために角ガラスの歪み点温度より若干上の温度に加熱（１００℃／ｈｒ）し、保持（３時間）後、徐冷（６０℃／ｈｒ）した。こうして表面の熱および加工歪みを完全に除去した状態にてその脆さを測定した。

【００４４】脆さの測定にはビッカース硬さ試験器を使用した。同装置により、ガラス表面に圧痕を打ち込み、前記の（１）、（２）式を用いてその圧痕の四角から発生するクラックの長さとビッカース圧子の押し込み荷重により脆さを算出した。

【００４５】押し込み荷重は５ｋｇ重とし、すべての例について脆さを測定した。また、密度については、試料の乾燥重量と水中での重量からアルキメデス法により算出した。測定にはマイクログラムまで測定可能な高精度の秤を使用し、有効数字５桁まで計算したのち最後の桁を四捨五入して４桁とした。

【００４６】表１、表２より本発明の組成範囲にあるガラスはすべて密度が２．４１０を超えて２．４７０ｇ／ｃｃ以下であり、かつ脆さ指標値ｂが$6700\,m^{-1/2}$以下、粘度が$10^2$ポイズとなる温度が１６００℃以下となっている。

【００４７】それに対し、その範囲外の比較例（例９、例１０）では密度は２．４７０ｇ／ｃｃ以下で、脆さ指

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標値Bは６６００$m^{-1/2}$以下となっているが、１０$^2$ ポイズとなる温度が１６００℃以上で溶解・成形性に難がある。比較例（例１１、例１２）では、１０$^2$ ポイズとなる温度が１６００℃以下で溶解・成形が容易であるが、密度は２．４７０ｇ／ｃｃを超えており、脆さ指標値Bが６６００$m^{-1/2}$を超えるため、耐擦傷性の改善が見られない。

【００４８】また、これらの例において密度と脆さは良い正の相関を示しており、密度が低下するにしたがって脆さ指標値も低下する、すなわち傷が付きにくくなっていることが分かる。

【００４９】さらに、最も低い脆さ指標値を示した例２のガラスにビッカース圧子を押し込んだときの亀裂発生荷重（荷重を徐々に増やしていくと、その荷重以上にお＊

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＊いて初めて圧痕の四角からクラックが発生する荷重）を求めると、９００ｇ重となった。通常のソーダライムガラスでは同一の方法で求めた亀裂発生荷重は２００ｇ重であり、脆さを改善することにより亀裂発生荷重を４．５倍まで高めることができた。これはガラスの実使用時強度低下の主要因がガラス製造後に表面に発生した傷によることを考えると、非常に大きい利点である。

【００５０】すなわち、本組成のガラスを使用することにより実使用時の表面傷による強度低下を低減でき、その結果商品の寿命を格段に伸ばし、またその信頼性を大幅に改善しうる。

【００５１】

【表１】

| | | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| 組成 | $SiO_2$ | 75.1 | 75.1 | 75.1 | 75.1 | 75.0 | 75.0 |
| | MgO | 9.4 | 9.4 | 10.4 | 11.4 | 13.4 | 14.4 |
| | CaO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | ZnO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $Li_2O$ | 15.5 | 14.5 | 13.5 | 6.5 | 5.5 | 5.0 |
| | $Na_2O$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $K_2O$ | 0.0 | 0.0 | 0.0 | 6.0 | 5.0 | 4.5 |
| | $Al_2O_3$ | 0.0 | 1.0 | 1.0 | 1.0 | 1.1 | 1.1 |
| $RO+R_2O$ | | 24.9 | 23.9 | 23.9 | 23.9 | 23.9 | 23.9 |
| $RO/R_2O$ | | 0.61 | 0.65 | 0.77 | 0.91 | 1.28 | 1.52 |
| 密度(g/cc) | | 2.424 | 2.422 | 2.426 | 2.426 | 2.433 | 2.437 |
| B ($m^{-1/2}$) | | 6200 | 6100 | 6300 | 6300 | 6300 | 6400 |
| $10^2$poise (℃) | | 1264 | 1288 | 1288 | 1352 | 1356 | 1358 |
| $10^4$poise (℃) | | 826 | 851 | 864 | 951 | 966 | 974 |

【００５２】

【表２】

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| | | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|
| 組成 | $SiO_2$ | 77.0 | 77.9 | 80.3 | 83.0 | 58.9 | 67.0 |
| | MgO | 14.1 | 9.5 | 0.0 | 3.3 | 0.0 | 0.0 |
| | CaO | 0.0 | 1.0 | 9.4 | 0.0 | 4.8 | 10.0 |
| | ZnO | 0.0 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $Li_2O$ | 5.0 | 10.6 | 0.0 | 0.0 | 0.0 | 0.0 |
| | $Na_2O$ | 1.1 | 0.0 | 10.3 | 10.3 | 16.1 | 15.0 |
| | $K_2O$ | 2.8 | 0.0 | 0.0 | 0.0 | 0.0 | 5.0 |
| | $Al_2O_3$ | 0.0 | 0.0 | 0.0 | 3.4 | 20.2 | 3.0 |
| $RO+R_2O$ | | 23.0 | 22.1 | 19.7 | 13.6 | 20.9 | 30.0 |
| $RO/R_2O$ | | 1.58 | 1.09 | 0.91 | 0.32 | 0.30 | 0.50 |
| 密度(g/cc) | | 2.430 | 2.430 | 2.431 | 2.347 | 2.488 | 2.522 |
| B　$(m^{-1/2})$ | | 6300 | 6300 | 6100 | 4000 | 6800 | 7000 |
| $10^3$poise (℃) | | 1390 | 1450 | 1786 | 2314 | 1338 | 1387 |
| $10^4$poise (℃) | | 1033 | 985 | 1179 | 1366 | 976 | 1066 |

【００５３】

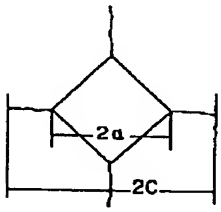
【発明の効果】本発明のガラスは溶融法によって生産性良く製造できるとともに、これを使用することにより実使用時の表面傷による強度低下を低減でき、その結果商品の寿命を格段に伸ばし、またその信頼性を大幅に改善＊20＊できる。

【図面の簡単な説明】

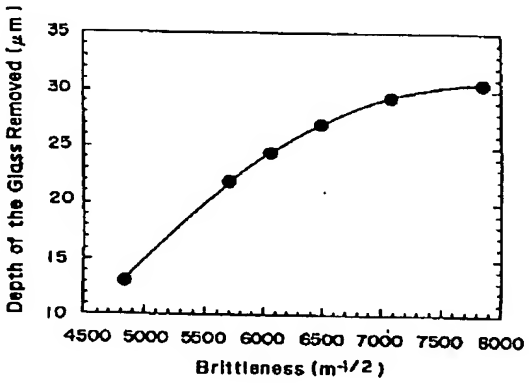
【図１】本発明における脆さの定義を説明する説明図

【図２】脆さ指標値Ｂとサンドブラストによる摩耗量との関係を示すグラフ

【図１】




【図２】

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フロントページの続き

| (51)Int.Cl.⁶ | 識別記号 | 庁内整理番号 | ＦＩ | 技術表示箇所 |
|---|---|---|---|---|
| Ｃ０３Ｃ　4/00 | | | Ｃ０３Ｃ　4/00 | |

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